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Enhancing biological treatment of dye wastewater with zero-valent iron

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Abstract−Pretreatment of authentic industrial dye wastewater with zero-valent iron (ZVI) was evaluated using a bench-scale integrated anaerobic-aerobic (ZVI-AO) biological treatment system. Average ADMI (American Dye Manufacturers' Institute) value of dye wastewater was reduced from 245 to 107 units with ZVI column pretreatment. Subsequent treatment of ZVI column effluent by a continuous AO process further reduced the ADMI values to 18-39, resulting in overall decolorization efficiency of 78-89%. A control AO system without ZVI pretreatment, which was operated in parallel, achieved just 44-69% of ADMI removal efficiency. In addition, the ZVI integrated system yielded effluents with much lower COD and BOD concentrations than the control system. The aerobic batch respiration tests confirmed that ZVI treatment transformed the recalcitrant dye compounds to slowly biodegradable fractions, thus enhancing the overall biodegradability of dye wastewater.

Keywords: Zero-valent Iron, Decolorization, ADMI Value, Anaerobic-aerobic Process, Biodegradability

INTRODUCTION

In Korea, dye wastewater typically undergoes physico-chemical pretreatment in individual dyestuff industry or public-owned industrial wastewater treatment facilities prior to being discharged to domestic wastewater treatment plants. However, sufficient color removal cannot be accomplished in traditional wastewater treatment processes because of the recalcitrant characteristic of dye wastewater [1,2].

Recently, the application of zero-valent iron (ZVI, Fe^0) for the removal of dye has received a great deal of attention because dyes may be readily reduced by ZVI, which has been verified for several azo dyes [3-5]. Nam and Tratnyek [6] observed that nine kinds of azo dyes showed first-order decomposition rate with reductive reaction by ZVI. Lin et al. [4] also investigated the decreasing rate of AB24 azo dye concentration which followed pseudo-first-order kinetics when it was contacted with nano/micro sized ZVI. Through the pretreatment of orange G and orange II with ZVI, biodegradability improvement could be achieved together with decolorization of the dyes [7,8].

Although the ZVI induced reduction of azo dyes may have its potential application in the decolorization of dye wastewater, few studies have applied the ZVI to real dye wastewater treatment. Ma and Zhang [3] observed 10.2 and 28.6% increase in color removal efficiency with the applications of iron shavings in pilot- and full-scale treatment of real dye wastewater. They also found that BOD and COD removal efficiencies were also increased and suggested that the iron shavings may have improved biodegradability of the dye wastewater.

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Manufacturing dyestuffs generally use a number of dyes from different chemical classes, which results in wastewaters with highly varying composition and chemical characteristics [9,10]. Nonetheless, many researchers have used synthetic dye wastewaters to investigate the potential treatment technologies [4,5,7,11]. The dye concentrations examined in these artificial wastewater studies varied widely from 0.01 to 7 g/L [10]. In this study, we examined the application of ZVI technology for the treatment of real dye wastewater treatment using bench-scale reactors. Since the experiment was conducted with the real dye wastewater, the degree of treatment in the test systems was assessed in terms of absorbance rather than dye concentration to investigate the decolorization behavior. In addition, the effects of ZVI treatment on the biodegradability of dye wastewater and its impact on subsequent biological treatment processes were investigated.

MATERIALS AND METHODS

1. Dye Wastewater

Dye wastewater used in this study was the effluent from an industrial wastewater treatment plant in Korea. This plant receives wastewaters from over 100 dyeing and finishing industries and utilizes chemical coagulation as the core treatment technology. The effluent is discharged to a nearby domestic wastewater treatment plant and goes through a traditional biological treatment processes along with domestic wastewater. The influent flow rate of the domestic wastewater treatment plant is 100,000-120,000 m^3/d and about 50% of the flow was from the industrial wastewater treatment plant. The analysis of chemical composition of dye wastewater is nearly impossible because daily variation of dyestuffs used in dyeing industries is very high. Instead of direct analysis of chemical composition of dye wastewater, COD, BOD, SS, TN and TP were analyzed for characterizing the dye wastewater. Organic concentration of the dye waste-

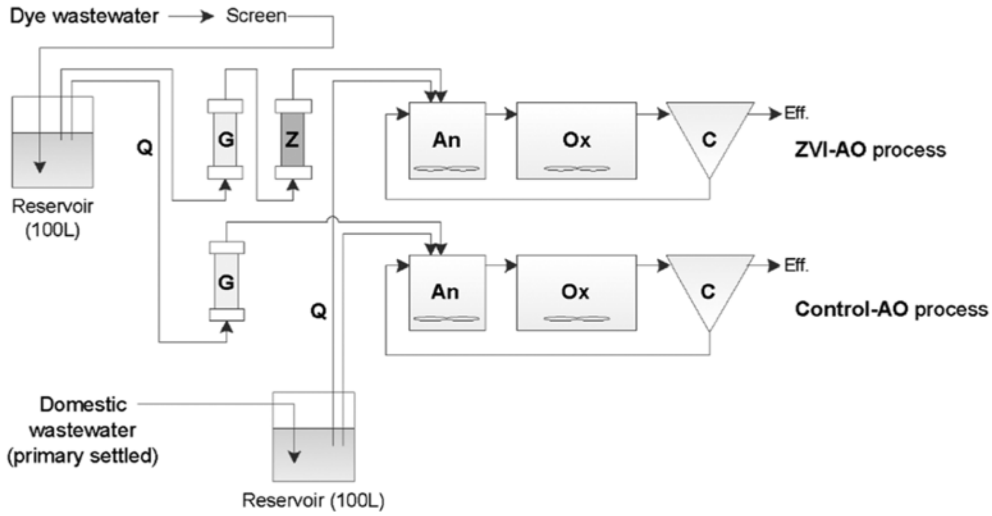

Fig. 1. Schematic of ZVI-AO and control-AO process.

G. Guard column (empty bed vol.: 4 L) An. Anaerobic reactor (20 L) C. Clarifier (15 L)
Z. ZVI column (empty bed vol.: 4 L) Ox. Aerobic reactor (40 L) Q. 20, 30, 40 Ld^{-1} (phase I, II, III, respectively)

water was 198-344 mg TCOD/L and 107-156 mg BOD_5/L. Suspended solids (SS), total nitrogen (TN) and total phosphorus (TP) concentration of the wastewater was 45-78, 12-27 and 0.3-2.6 mg/L, respectively.

2. ZVI-AO Process

Anaerobic azo dye decolorization is a reliable process, where dye might act as an acceptor of electrons supplied by carriers of the electron transport chain [1]. Alternatively, decolorization might be attributed to non-specific extracellular reactions occurring between reduced compounds generated by the anaerobic biomass [2]. From these points of view, we adopted an anaerobic-aerobic (AO) system as a biological process for dye wastewater decolorization.

A bench-scale anaerobic-aerobic (AO) process combined with a ZVI column (ZVI-AO) was constructed in a wooden shed near the grit chamber of the domestic wastewater treatment plant. The bench-scale system was operated for ten months including one month acclimation period. A schematic of ZVI-AO and control AO process is shown in Fig. 1.

A control AO process was also operated in parallel to compare the treatment efficiency and to characterize the beneficial effects of ZVI. Total influent flowrate was 40 (phase I), 60 (phase II) and 80 (phase III) L/d and dye wastewater consisted of about 50% (20, 30 and 40 L/d at each phase, respectively) of total influent flowrate. The hydraulic retention times (HRTs) of anaerobic and aerobic reactor was 6-12 h and 12-24 h, respectively.

As shown in Fig. 1, dye wastewater was pumped into the ZVI column in upward mode prior to biological treatment in ZVI-AO process. A control AO system without ZVI column was operated in parallel. Empty bed volume and empty bed contact time (EBCT) of the ZVI column was 4 L and 2.4-4.8 h, respectively. The ZVI column was packed with a mixture of ZVI and sand at a 1 : 1 (v/v) ratio. The ZVI used in this study was commercially available high-purity iron granules (purity>99.9%, Fluka) and sieved with 14-30 mesh before use. The sand was also sieved with same mesh and effective size (diameter) was 0.6-1.4 mm. Specific surface area of the ZVI particles was determined with a Micromeritics ASAP 2010 chemisorption surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). The BET surface area of the ZVI particles was in the range of 1.24-1.53 m^2/g.

A guard column (Fig. 1) packed with only sand was installed prior to ZVI column to remove particulate matter in dye wastewater. Guard columns were backwashed when the column effluent was decreased to below 95% of designed flowrate.

3. Biodegradability Test

To evaluate the effect of ZVI on biodegradability of dye wastewater, batch oxygen uptake rate (OUR) tests were conducted to estimate readily biodegradable COD (RBCOD, S_S) and slowly biodegradable COD (SBCOD, X_S) concentration of wastewater [12-14]. OUR measurement apparatus consisted of an open aerobic batch reactor (8 L) and an air tight DO measuring chamber (480 mL) as shown in Fig. 2. The feed solutions for aerobic batch OUR tests were taken from ZVI column influent and effluent (Fig. 1). Seed sludge for OUR batch test was taken from ZVI-AO process after sufficient acclimation period (over two sludge ages). To inhibit nitrification, allythiourea (ATU) was added to a concentration of 20 mg/L as described by Dircks et al. [15].

The OUR tests were conducted at a temperature of 20±1 °C. Dis-

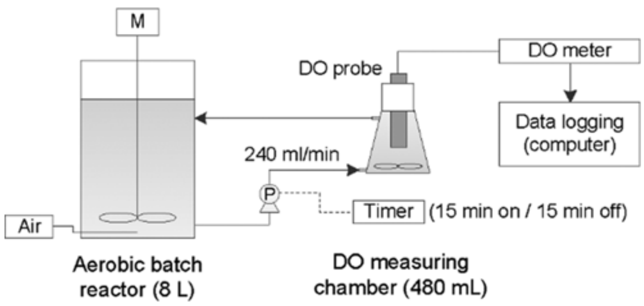

Fig. 2. An experimental set-up for OUR batch test.

solved oxygen (DO) concentration was recorded every 30 sec with an oxygen electrode (YSI 5739 field probe connected to YSI model 58 DO meter) and a computer. When the measuring period reached 15 min, the mixed liquor in the measuring chamber was replaced with fresh samples from the aerobic batch reactor at a flowrate of 240 mL/min. At the same time, the mixed liquor in the measuring batch was recycled back to the aerobic reactor. The recycling was continued for 15 min, and the recycle pump, which was controlled by a timer, was stopped at this time as well as measuring period started again simultaneously. Oxygen measurements were logged by a computer and respiration rates were then calculated by linear regression of all the obtained dissolved oxygen (DO) data.

4. Analytical Methods

Absorbance of the wastewater solution was determined by UV-spectrophotometer (DR/4000U, Hach) with a detection range of 350-700 nm. All samples were filtered through 0.45 mm membrane filter and stored below 4 °C before the analysis of absorbance. ADMI (American Dye Manufacturers' Institute) value was determined using tristimulus filter (438, 540, 590 nm) and Adams-Nickerson methods as described by Allen et al. [16]. The ADMI measurement can be used for determining the color of samples. The method involves measuring the absorbance of samples after filtration at sets of 10 or 30 wavelengths depending on the accuracy required to generate the CIE (Commission International de l'Eclairage) tristimulus values, X, Y, and Z. These are converted by the use of published tables to values called Munsell values [10]. From the Munsell values the Adams-Nickerson color difference (DE) is calculated from an equation. The DE values of a series of APHA platinum-cobalt standards is plotted against the corresponding ADMI values to give a calibration plot and the DE value of samples read against this plot to obtain the ADMI value of the sample.

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were analyzed in accordance with the Standard Methods [17].

RESULTS AND DISCUSSION

1. Decolorization

Since APHA (American Public Health Association) suggests tristimulus value method to evaluate dye wastewater and this method adopts the interval of absorbance spectra from 400 to 700 nm [17], we selected a similar range of absorbance spectra (from 350 to 700 nm) of dye wastewater which was scanned to examine the effect of decolorization process. Fig. 3(a) shows the absorbances of influent dye wastewater and ZVI column effluent at the end of each Phase. At phase I and III, the highest absorbance can be found at minimum wavelength. Nam and Tratnyek [6] also reported the highest absorbance in the same range for a dye manufacturing wastewater. At Phase II, an absorbance peak was observed around 550 nm, which is similar to the absorbance pattern described by O'Neill et al. [10]. They also reported that absorbance of typical site effluent dropped after 600 nm. However, this phenomenon did not occur in this study as shown in Fig. 3(a).

Although volumetric loading of dye wastewater was increased from 20 to 40 L/d (EBCT was decreased from 4.8 to 2.4 hr), ZVI column showed stable decolorization performance during the nine-month operation (Fig. 3(b)). Greater than 60% of absorbance was decreased in all ranges of wavelengths scanned. In bench and pilot scale tests with industrial dye wastewater, Ma and Zhang [3] observed 62-69% decolorization efficiency with iron shavings with EBCT of 2-2.25 hr. Quantification of color of dye wastewater in terms of ADMI color values is more useful than individual dye concentrations because different dyes give rise to different intensities of colors [10]. Therefore, we adopted ADMI values for evaluating the decolorization by ZVI column and ZVI-AO process (Fig. 4). ADMI values of influent dye wastewater ranged from 204 to 292 units (Fig. 4(a)), which is much lower than typical values reported in the literature (1,000-1,500 ADMI units) [10] because influent dye wastewater in this study already went through chemical pretreatment (coagulation).

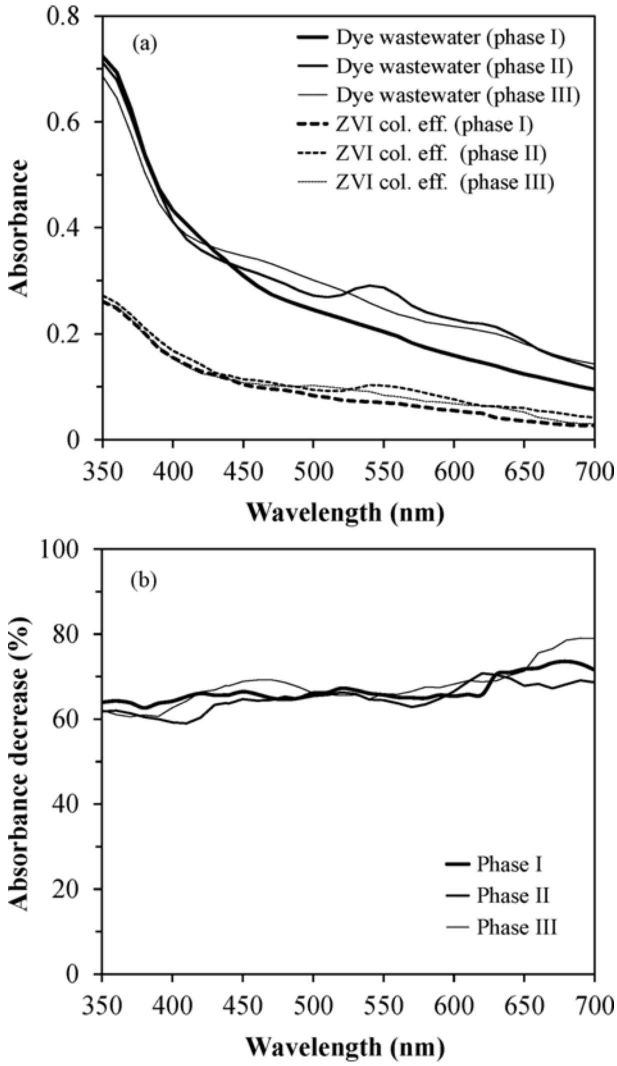

Fig. 3. Absorbance of influent dye wastewater, ZVI column effluent (a) and absorbance decrease (%) before and after ZVI column (b) at 89 days (phase I), 175 days (phase II) and 272 days (phase III) of operation (absorbance scanning interval: 10 nm).

Decolorization of dye wastewater by ZVI column was evaluated by comparing the ADMI values of dye wastewater and ZVI col-

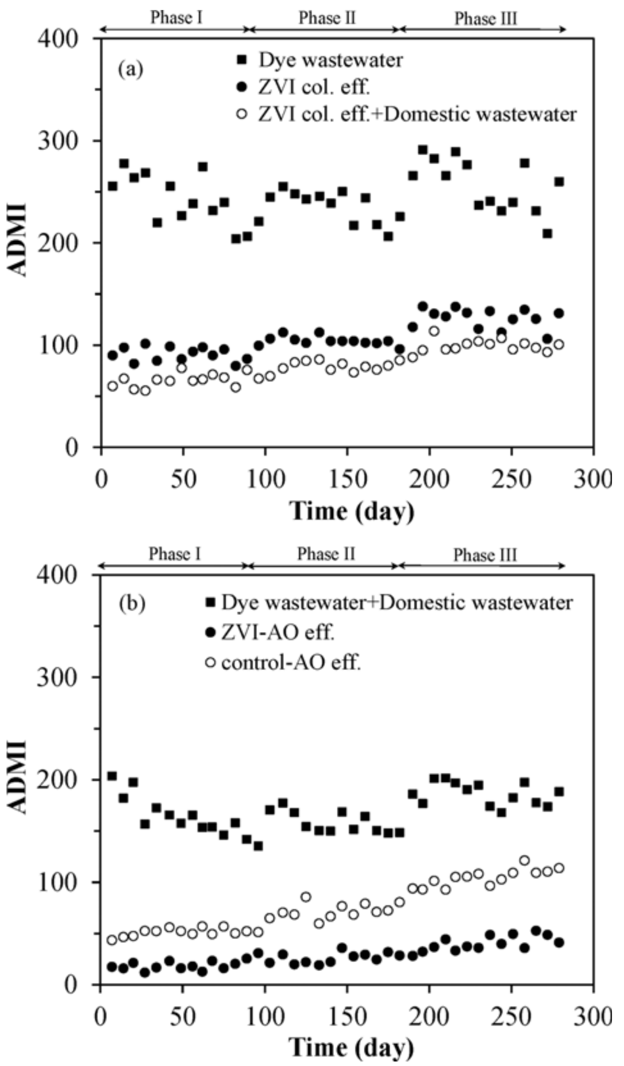

Fig. 4. Decolorization behavior of ZVI column (a) and both AO processes (b).

Table 1. Decolorization (ADMI color removal) efficiencies (average± deviation, %)

	ZVI column	ZVI-AO process	Control-AO process
Phase I	62.4±2.8	88.7±3.0	68.6±5.2
Phase II	55.5±2.7	83.2±3.7	55.7±5.3
Phase III	51.2±3.4	78.4±4.6	43.9±5.1

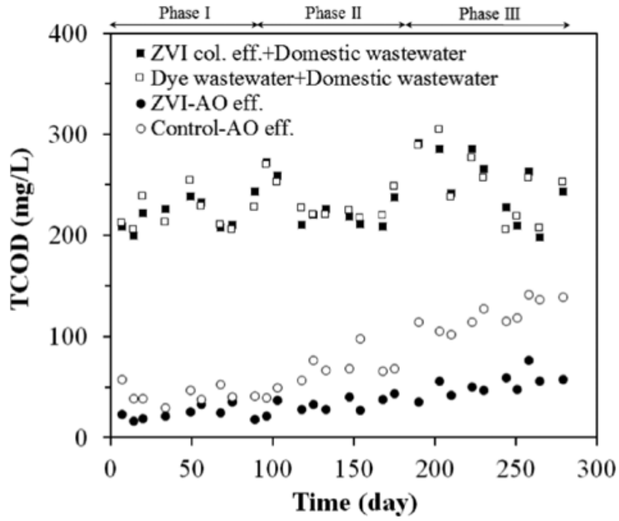

Fig. 5. TCOD concentration in the influent and effluent of the AO processes.

umn effluent. Fig. 4(a) shows substantial decolorization of dye wastewater by ZVI column over 280 days of operation although a little decrease in decolorization efficiency occurred at phase II and III due to higher volumetric loading of dye wastewater. Decolorization efficiency of ZVI column at each phase is summarized in Table 1. Removal of ADMI color units decreased by only 11.2% in spite of doubled loading rate at phase III.

Decolorization by the AO processes was examined by comparing the ADMI values between the influent (1 : 1 mixture of dye wastewater and domestic wastewater by v/v) and the effluents from the AO processes (Fig. 4(b)). ZVI-AO process resulted in about 20 (phase I) - 35 (phase III) % higher decolorization efficiency than control AO process. Decolorization efficiency of the control process deteriorated substantially after phase I and the effluent ADMI values at phase III reached the levels higher than the color values achieved with just ZVI column. In addition, the extent of decolorization observed in the biological portion of ZVI-AO process was greater than that of control AO system, suggesting that the biodegradability of dye wastewater was enhanced after contact with ZVI. Similar observation was reported by Ma and Zhang [3] and Saxe el al. [8].

2. Organic Removal

During the ten-month experimental period, total COD (TCOD) concentration of dye wastewater varied from 198-344 mg/L. Differences in TCOD concentration of influent wastewater to both

Table 2. Summary of organic concentration in both AO processes (average, mg/L)

	ZVI-AO influent*			Control-AO influent**			ZVI-AO effluent			Control-AO effluent		
	TCOD	SCOD	BOD_5	TCOD	SCOD	BOD_5	TCOD	SCOD	BOD_5	TCOD	SCOD	BOD_5
Phase I	220.8	125.8	124.6	221.6	132.6	105.8	23.7	24.6	13.3	42.5	26.8	14.6
Phase II	229.2	132.4	132.5	233.1	138.3	134.7	32.7	27.4	15.8	65.3	35.4	16.4
Phase III	251.0	138.6	148.4	250.4	142.8	135.4	52.6	36.5	14.2	121.6	59.3	19.8

*Mixture of ZVI column effluent and domestic wastewater

**Mixture of dye and domestic wastewater

AO processes were small (<23 mg/L) because ZVI treatment had minimal effect on total organic concentration (Fig. 5).

Average TCOD, SCOD and BOD_5 concentration at each phase are summarized in Table 2. All three organic indicators showed that the removal of organic materials was consistently higher in the ZVI-AO system than the control AO process. This result again suggests that the pretreatment of dye wastewater enhanced the mineralization of organic materials in the subsequent biological process. Enhancement of dye biodegradation with ZVI treatment has been reported by several researchers. Perey et al. [7] showed that the biodegradability of orange-G dye was enhanced after reduction by ZVI through respirometric analysis. In subsequent experiments with ZVI-activated sludge process, Saxe et al. [8] demonstrated that the integrated system was able to decolorize azo dye solutions and yielded effluents with lower total organic carbon concentrations than control system without ZVI pretreatment. Ma and Zhang [3] also demonstrated that organic removal efficiency was increased with ZVI pretreatment of real industrial dye wastewater.

3. Biodegradability Enhancement

The OUR test results for dye wastewater samples obtained before and after ZVI column at phase I are shown in Fig. 6. The OUR plots showed two distinctive linear regions and the slope of initial decrease in OUR values was greater than the slope of the second linear plot. The first part may be attributed to the rapid consumption of readily biodegradable COD (S_S). When S_S is depleted, the slope of OUR curves decreases and the OUR is most likely influenced by the concentration of slowly biodegradable COD (X_S).

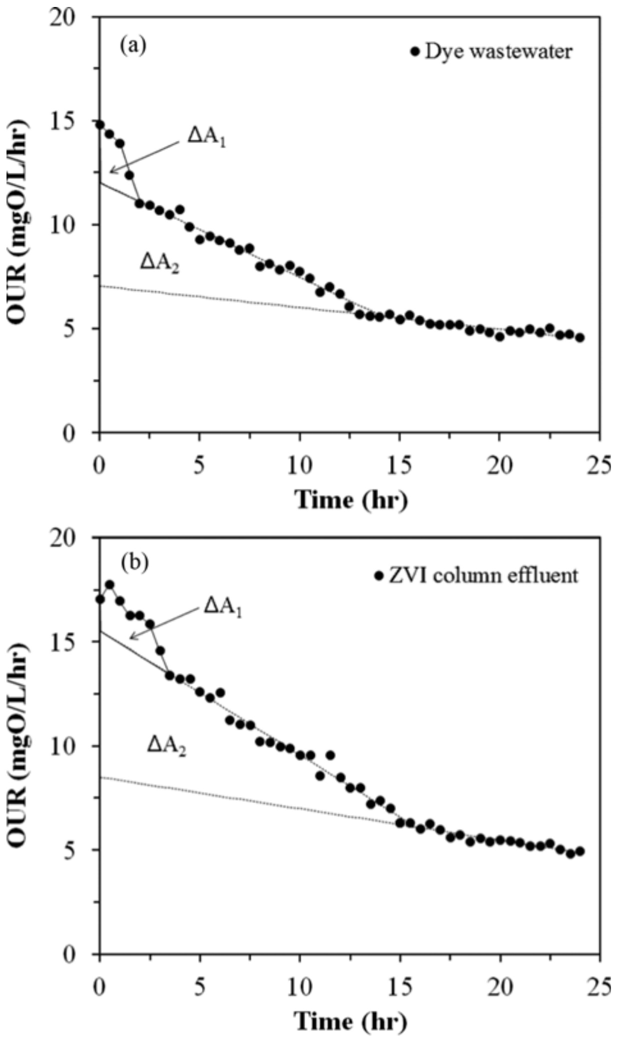

Fig. 6. Batch OUR data for dye wastewater (a) and ZVI column effluent (b) at phase I.

From the OUR graph, S_S and X_S values can be calculated as follows [12-14]:

$$S_S = \frac{\Delta A_1}{1 - Y_H} \cdot \frac{1}{f} \tag{1}$$

$$X_S = \frac{\Delta A_2}{1 - Y_H} \cdot \frac{1}{f} \tag{2}$$

where, ΔA_1=Area between initial OUR data and the upper regression line
ΔA_2=Area between the upper and lower regression line
Y_H: heterotrophic yield coefficient
f: volume fraction of the feed solution (0.9 in this study)

Y_H value was assumed to be 0.65 which was reported by Yu et al. [14] for an activated sludge process treating textile dyeing wastewater. Volume fraction of the feed solution (influent and effluent of ZVI column) was 0.9 and the remaining fraction (0.1) was by seed solution. The calculated values of S_S and X_S from phase I data for dye wastewater and ZVI column effluent are presented in Fig. 7.

The difference in S_S values between the dye wastewater and ZVI column effluent was minimal, suggesting that ZVI reduction process does not transform the dye materials to readily biodegradable by-products. Similarly, Pandey et al. [1] reported that by-products of dye decolorization were not readily utilized by microorganisms. On the other hand, slowly biodegradable concentration (X_S) was increased dramatically after ZVI treatment (from 110 to 176 mgCOD/L), indicating that the biodegradability of recalcitrant dye wastewater greatly enhanced by ZVI treatment. Similar trend observed with the subsequent phases as shown in Fig. 7.

Increase in S_S concentrations after ZVI treatment was minimal at all phases (Fig. 7). Previous studies indicated that iron metal can rapidly reduce azo functions in dye molecules, yielding aromatic

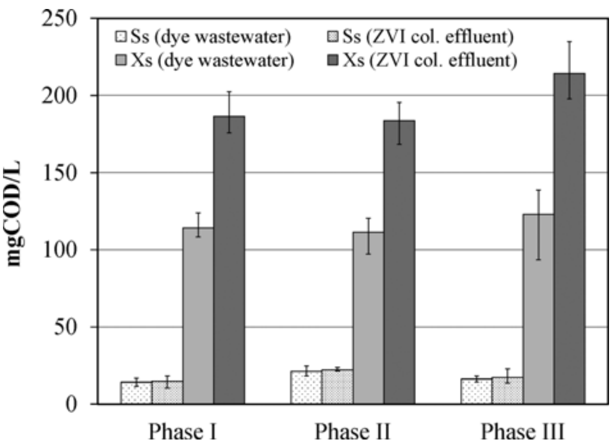

Fig. 7. Average S_S and X_S concentration at each phase.

amines as products [6,7]. Saxe et al. [8] showed that treatment of azo dyes (orange G and orange I) produces aromatic amines such as aniline and sulfanilic acids, which are more amenable to aerobic degradation than the recalcitrant parent compounds. Even though ZVI treatment did not transform the dye compounds to readily biodegradable products, substantial increase in X_S concentration after ZVI treatment clearly demonstrated the enhancement of biodegradability enhancement of dye wastewater.

CONCLUSIONS

(1) ZVI column pretreatment with 2.4-4.8 hr EBCT reduced ADMI values of industrial dye wastewater by 51-62%. Integration of ZVI column to a continuous AO treatment process enabled additional reduction in ADMI values.

(2) In spite of increased volumetric loading of dye wastewater (from 20 to 30 and 40 L/d), the ZVI integrated AO process showed over 78% ADMI removal efficiency. On the other hand, decolorization efficiency in control system without ZVI pretreatment gradually deteriorated at higher loading conditions.

(3) The ZVI integrated system yielded effluents with much lower COD and BOD concentrations than the control system. The aerobic batch respiration tests confirmed that ZVI treatment transformed the recalcitrant dye compounds to slowly biodegradable fractions, thus enhancing the overall biodegradability of dye wastewater.

(4) The construction and successful operation of the integrated ZVI-AO system confirmed that ZVI pretreatment can be a feasible option for treatment of a continuous stream of dye-laden wastewaters.

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